

New Solid Amine Sorbents

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Carbon Sequestration Meeting - May 2003



Overview

- Goals**

- To develop a cost efficient process for the capture of CO₂.

- Objective**

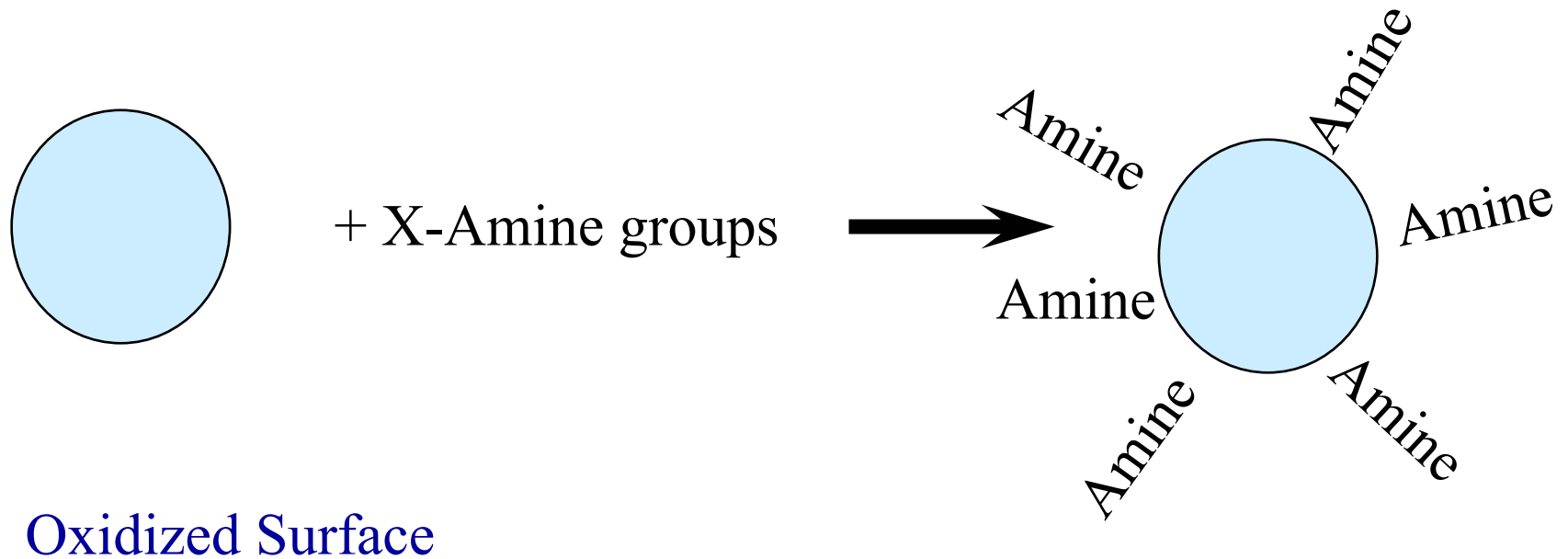
- To develop low-cost solid sorbents for the capture of CO₂ from flue gas streams

- Technical Challenges**

- To reduce the energy intensity of current capture processes (e.g.. MEA process)
 - To improve the capture capacity of sorbents
 - To produce affordable solid sorbents for the capture of CO₂
 - To improve the mass and heat transfer parameters
 - To increase the available contact surface
 - To reduce the corrosion problems



Chemical Treatments

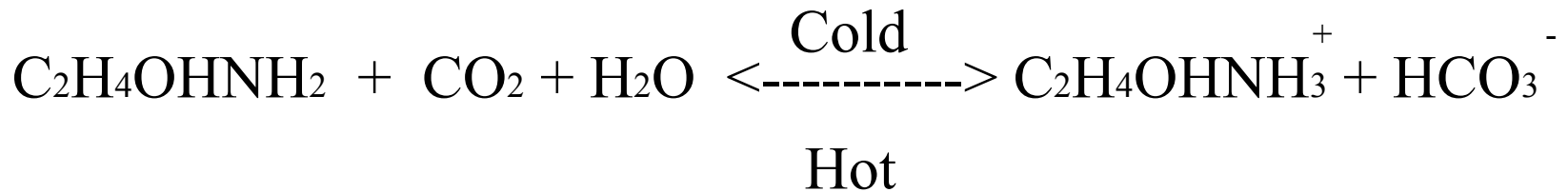


Potential Applications

- **Fossil-fuel power generation plants contribute about 1/3 of anthropogenic CO₂ emissions**
- **Power generation point sources**
 - Pulverized coal combustion plants
 - Advanced power system
- **Capture step**
 - Post-combustion
 - Pre-combustion
- **Storage step in carbon sequestration requires concentrated CO₂**
- **Natural gas clean up and Life support systems**



Typical Chemical Stripping Process

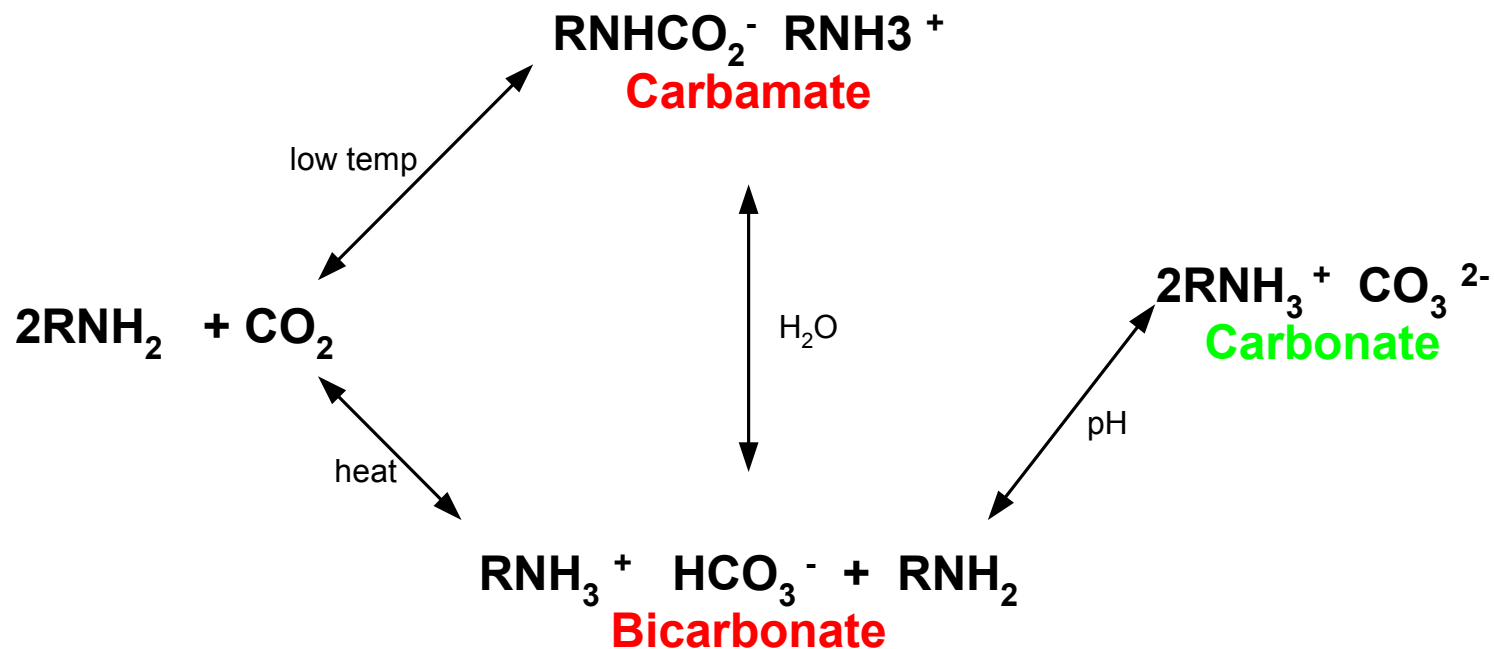


Typical adsorption process is determined by the available gas/liquid interaction surface. Therefore, a large amount of liquid is needed for capture a small amount of gas.

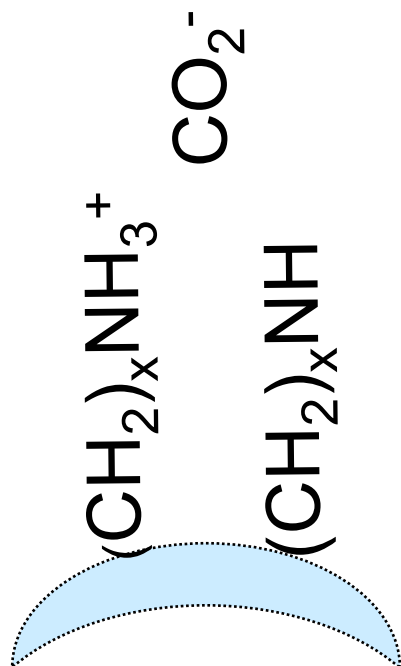
Energy intensive



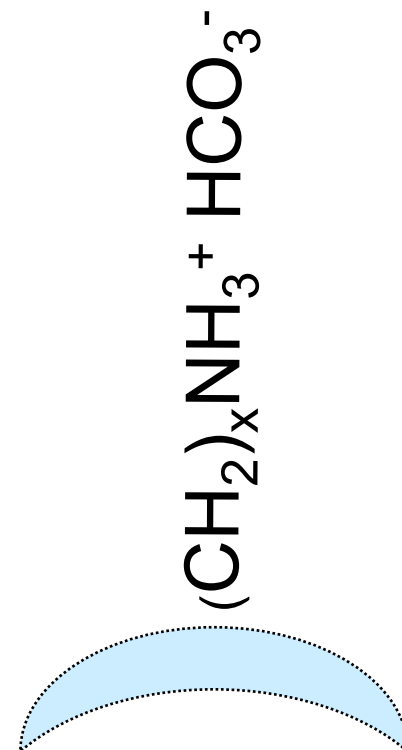
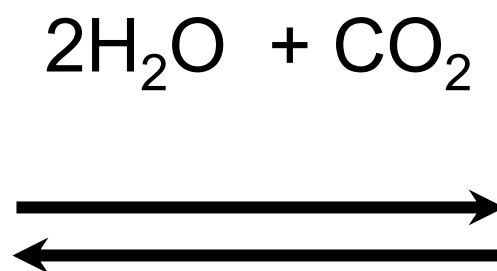
Proposed Reaction Sequence



Hook, R. J., *Ind. Eng. Chem. Res.*, **1997**, 36, 1779 -1790

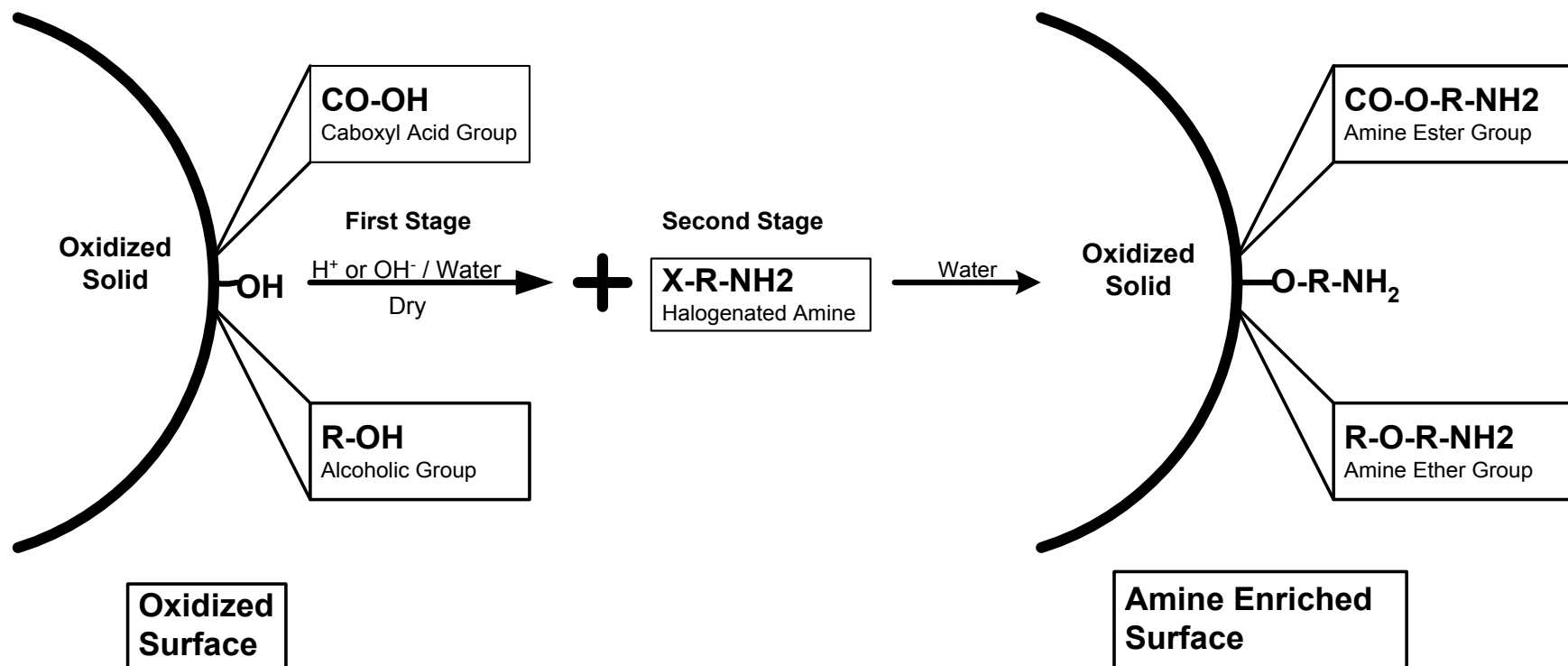


carbamate

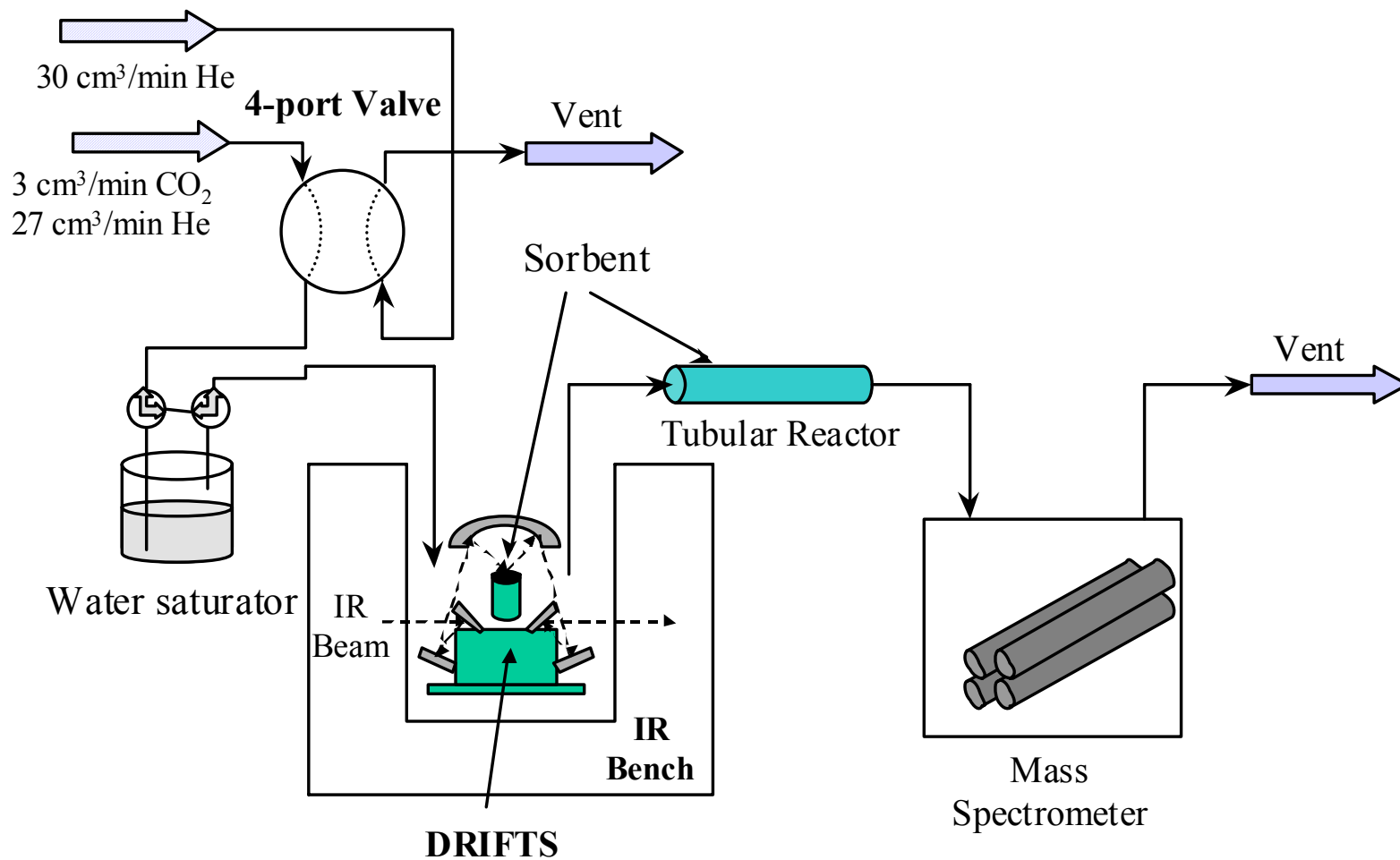


bicarbonate

Amine Treatment of Solid Substrates in Aqueous Media



US Patent 6,547,854 - 4/15/2003



Experimental TPD/FTIR Procedure

- 15 mg in FTIR and 115 mg in TPD reactor
- Outgas in He for 4 hrs.
- Ambient T, 10 % CO₂ in/He
- Ambient T, switch to CO₂/H₂OHe
- Ambient T, switch to H₂O/He to remove CO₂
- TPD, 10 °C/min. to 60 or 120 °C and hold for 30 min. in He



Initial Results

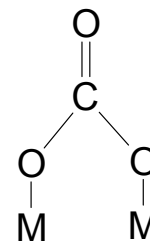
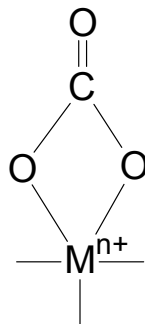
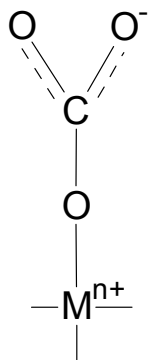
- **Modified fly ash derived carbon with 10^{-3} M of 3-chloropropylamine HCL (CPAH) and 10^{-1} M KOH**
 - 95 Fly ash carbon concentrate
 - 95A CPAH and KOH
 - 95B KOH only
 - 95C CPAH only
- **Tested prepared samples**
 - In-situ FTIR (DRIFT) to observe the surface absorption and adsorption/desorption states
 - TPD with on-line MS to monitor the desorbed gases



Samples	Desorbed amount	$\mu\text{mol/g sample}$
95	24	
95A	81	
95B	118	3-chloropropylamine hydrochloride
95C	174	
95C (regenerated)	140	

Proposed Species

Potential Adsorption of CO₂ onto a Solid Surface



Monodentate carbonate

Bidentate carbonate

Bridged bidentate carbonate

1530 – 1470 (ν_{as} COO⁻)

1530 – 1620 (ν C=O)

1620 – 1670 (ν C=O)

1300 - 1370 (ν_s COO⁻)

1270 – 1250 (ν_{as} COO)

1220 – 1270 (ν_{as} COO)

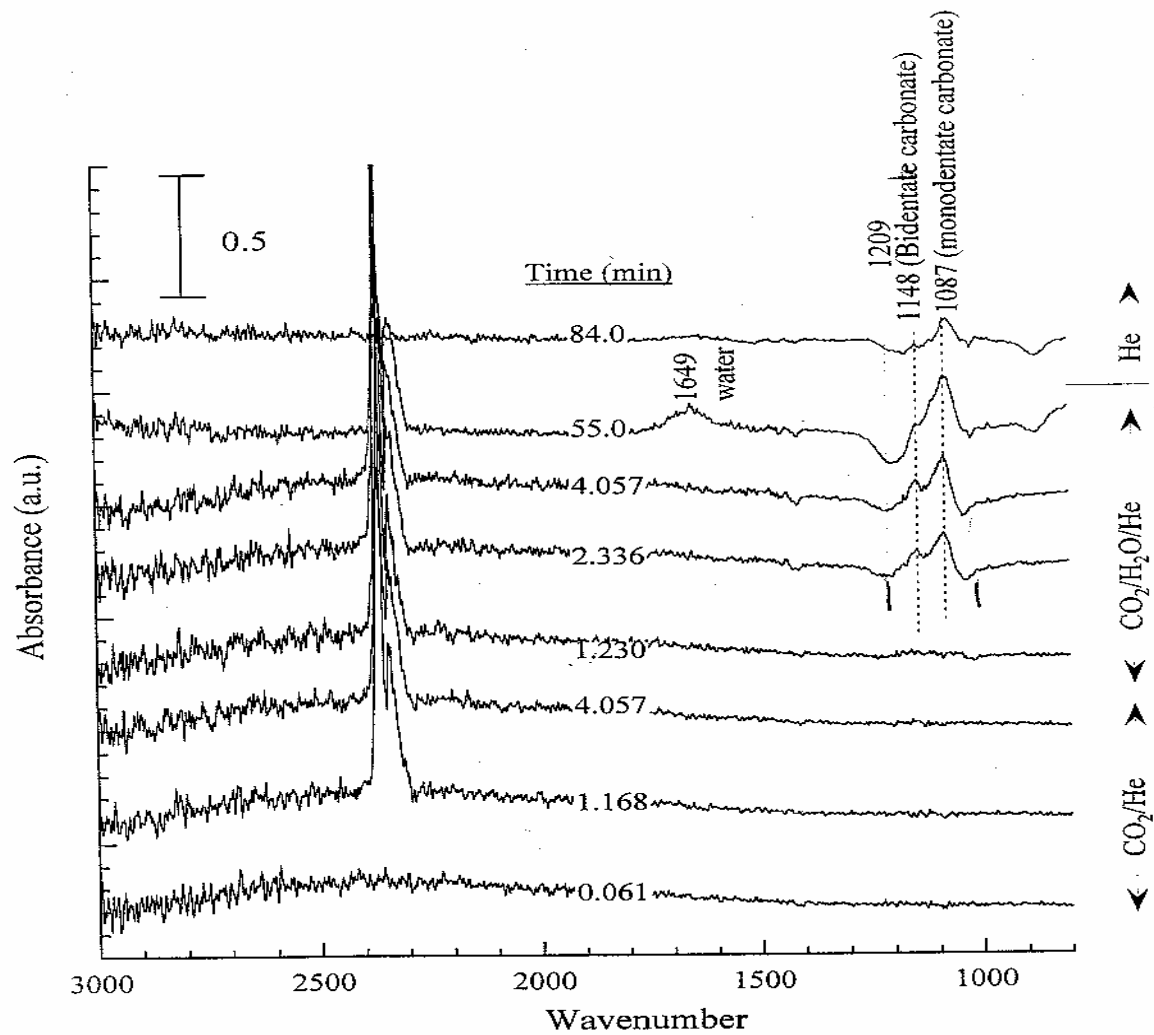
1080 – 1040 (ν CO)

1030 – 1020 (ν_s COO)

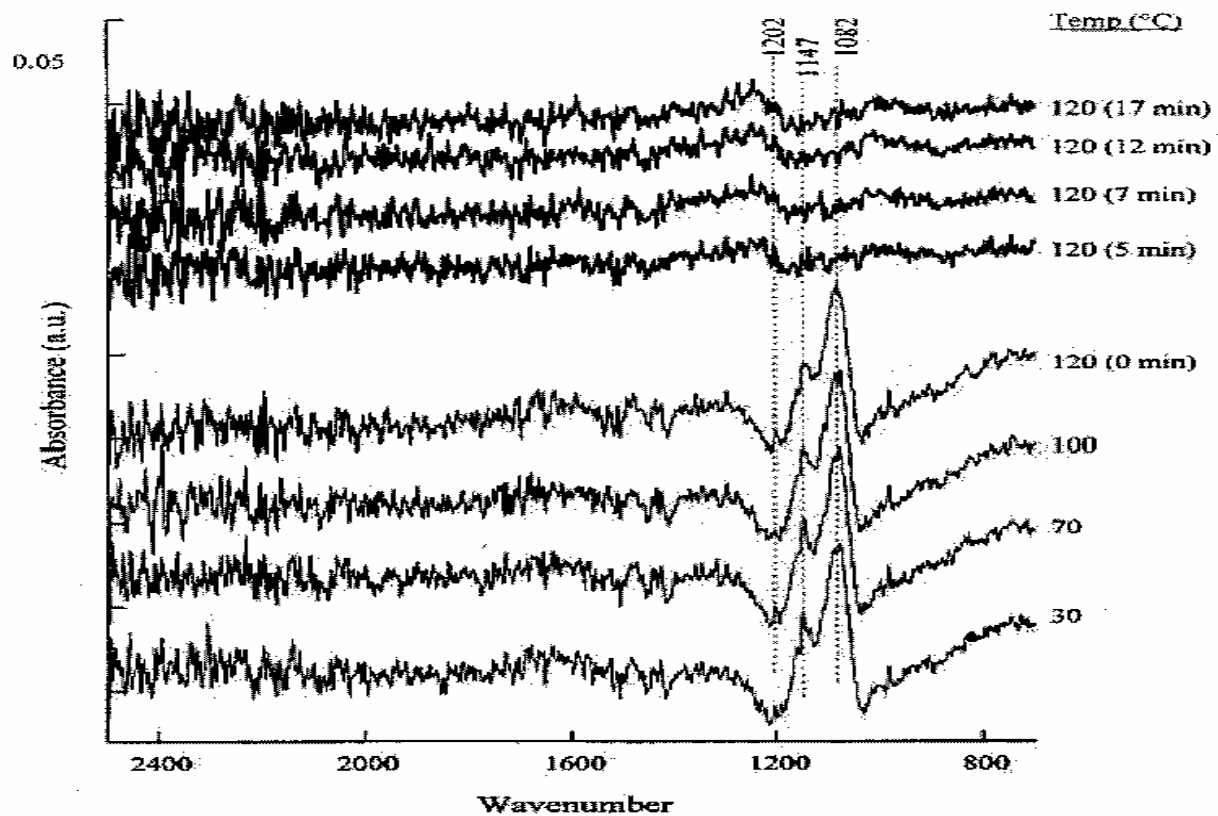
980 – 1020 (ν_s COO)

A.C.C.Chang, et al. "In-Situ Infrared Study of CO₂ Adsorption on SBA-15 Grafted with

γ-Aminopropyltriethoxy silane" *Energy & Fuel*, 17, pp. 468-73, 2003.



Adsorption profile of $\text{CO}_2/\text{H}_2\text{O}$ over 95°C



TPD profile over 95C

6/19/10

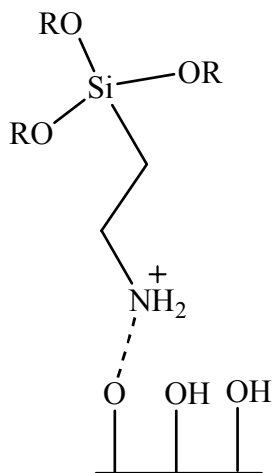
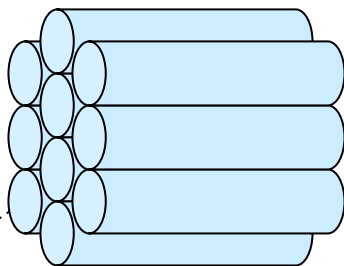
Figure 8

Activated Carbon Performance in CO₂/He/H₂O

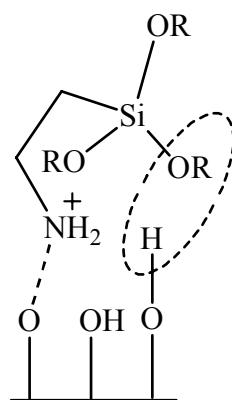
Sorbent and Treatment	μmol/CO ₂ Captured
Carbon feed	925.7
Carbon + OX	455.1
Carbon + OX + CPAH	1262.6
Carbon + OX + CPAH 1 st Regeneration	1021.7
Carbon + OX + CPAH 2 nd Regeneration	534.3



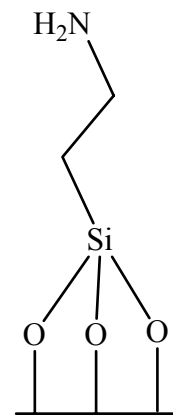
Preparation of the Silicon based Sorbent SBA-15 in Organic Media



Step 1



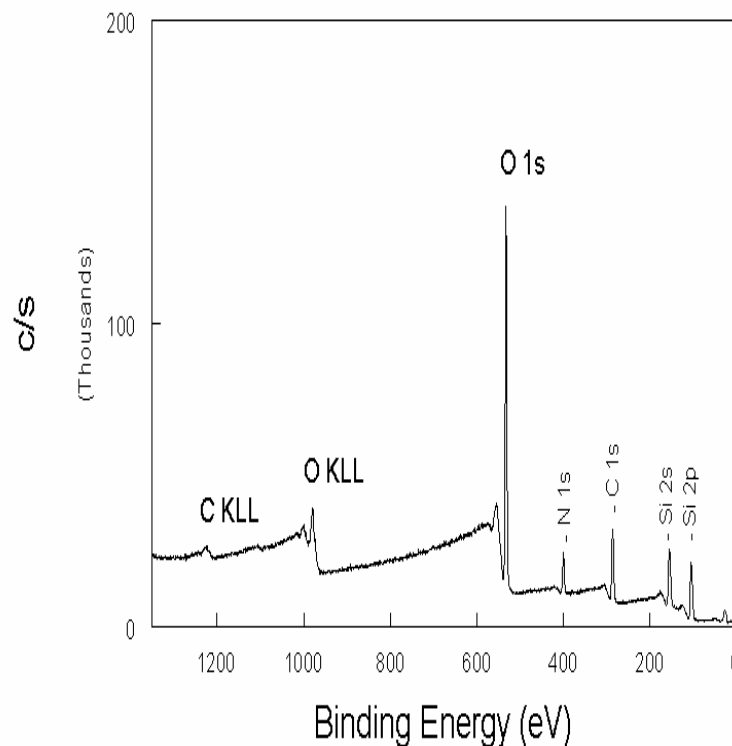
Step 2



Step 3

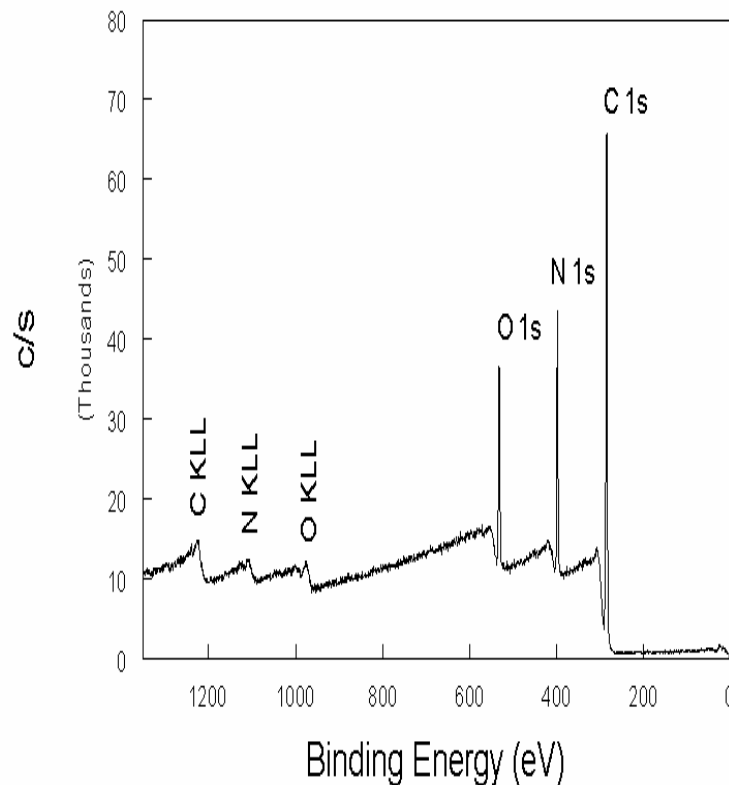
XPS Analysis of SBA-15 Sorbent

- SBA-15 Amine Sorbent.
- Nitrogen Content= **7.13%**
- Surface area = 227 m²/g



XPS Analysis of the Industrial Amine Solid Sorbent

- Industrial Amine Solid Sorbent.
- Nitrogen content= **17.73%**
- Surface area = 213 m²/g



Comparison of SBA-15 to Industrial Amine Solid Sorbent (IAS)

Sorbent	$\mu\text{mol/g CO}_2$ Captured	XPS % Nitrogen
SBA-15 fresh	2011.4	7.13
SBA-15 1 st regeneration	1908.5	NA
SBA-15 2 nd regeneration	1748.3	NA
IAS fresh	1603.9	17.73
IAS 1 st regeneration	1922.6	NA
IAS 2 nd regeneration	1528.1	NA



Summary of Sorbents Performance in CO₂/He/H₂O

Sorbent	Treatment	μmol/CO ₂ Captured	Surface Area m ² /g
Fly ash	Aqueous	157.2	27
Carbon	CPAH		
Carbon	Aqueous	939.5	1010
Ox + Am	CPAH		
TiO	Aqueous	1057.2	210
	Media		
SBA-15	Organic	1889.4	227
	Silicate		
IAS	Immobilized	1820.8	213



Conclusions

- **Demonstration of the implantation of amine groups on various substrates using both aqueous and organic reaction systems.**
- **Aqueous 3-chloropropylamine HCL reaction system requires addition investigation to improve its performance (fly ash carbon and activated carbon).**
- **Organic silicate reaction system produced a sorbent (SBA-15) with similar performance to the industrial amine solid (IAS) sorbent.**

